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(71)Applicant : **TITAN KOGYO KK**
(72)Inventor : **INOUE YOSHIHIRO**
CHIKAMORI YOJI
YAMAZAKI TAKANORI
MATSUMOTO SHOKI

(54) **PRODUCTION OF POWDERY FERROMAGNETIC METAL POWDER**

(57)Abstract:
PURPOSE: To obtain a fine metal grain excellent in coercive force, aspect ratio and dispersibility by absorbing a fatty acid on the surface of an acicular iron oxide grain made heat resistant, calcining and reducing the grain in a reducing atmosphere and reducing the grain with hydrogen.
CONSTITUTION: Goethite is surface-treated with the Si compd. and Al compd. as the heat resistance imparting agent, and then a fatty acid such as caprylic acid is adsorbed on the surface. The goethite is formed and dried or dried, disintegrated and regularly granulated, and the grain is calcined in a reducing atmosphere of gaseous nitrogen and reduced close to a magnetite composition. The grain is heated at about 350-550°C and reduced by a reducing gas such as gaseous hydrogen to obtain a ferromagnetic metal grain. The grain is then stabilized, as required.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the manufacturing method of the ferromagnetic metal powder for high-density magnetic recording media.
[0002]
[Description of the Prior Art]The magnetic metal powder produced by returning oxyiron hydroxide or iron oxide by reducing gas, for example, hydrogen, intrinsically, Compared with oxide stock magnetic powder, for example, gamma-Fe_2O_3 etc., high coercive force (Hc) and a big saturation magnetic moment (sigmas) are held, and it has the characteristic

outstanding as a charge of high-density magnetic-recording material, and is put in practical use by 8-mm videotape, DAT tape, etc. in recent years.
[0003]However, the demand to the densification of record, i.e., a high increase in power in a large frequency band, and low-noise-izing is recent years still stronger, and it is going to meet this demand by the miniaturization of particles, high-coercive-force-izing, and smoothing of the medium surface by improvement in dispersibility. For example, moreover, manufacture of magnetic metal powder with little coercive force to the sintered particle of 1600 to 2000 Oe is desired by a 0.1-0.15-micrometer particle.
[0004]Generally a vapor-phase-reducing method is used for manufacture of the magnetic metal powder which made the main ingredients these [Fe] which are called metal powder. However, the volumetric shrinkage which reaches also to about 47% eventually in connection with change and it of a crystal structure since a powder particle takes the reaction process of alpha-FeOOH->alpha-Fe $_2O_3$->Fe_3O_4-> alpha-Fe by this method happens, Particle shape collapses in the process of a transformation and the weld and sintering further between particles occur.
[0005]Then, the method of obtaining the magnetic metal powder which prevents the weld and sintering between particles and has the predetermined characteristic is studied variously, By returning, after carrying out the surface treatment of the raw material iron oxide with the salt of metal, such as P, Si, aluminum, Zn, Zr, Ti, and Bi, or hydroxide of those metal, The method of holding the skeleton of the magnetic powder which uses Fe obtained as the main ingredients good is indicated variously (in large numbers [for example, JP,48-79153,A, JP,51-5608,B, etc.]). By these methods, preventing weld between particles and sintering of the particle itself, and making a needlelike skeleton hold is proposed by processing the surface of iron oxide with metal salt or hydroxide, such as P, Si, aluminum, Zn, Zr, Ti, and Bi.
[0006]In the case of the metallic magnetic powder with a particle diameter of 0.1-0.15 micrometer in which demand grew, by these methods, needlelike nature fitness cannot be enough satisfied as magnetic powder for high-density magnetic recording media in recent years that it is hard to say.
[0007]When processed with a metaled salt or hydroxide, such as P, Si, aluminum, Zn, Zr, Ti, and Bi, reducibility was spoiled remarkably, and the temperature rise of reduced temperature and long time-ization of reduction processing were not able to be avoided further. In this case, if nickel is added, while reducibility will be improved and low-temperature-izing of reduced temperature and shortening of processing time will be attained, generally it is known that SFD will worsen. In order to avoid aggravation of SFD, refraining from use of nickel is in the situation where the bad surface treatment iron oxide of reducibility must be returned desirably therefore, and it needed the temperature rise of reduced temperature, and long time-ization of reducing time. Increase of reduced temperature is disadvantageous for maintenance of needlelike nature, and productivity cannot but fall by the increase in reducing time. In the case of the particle with a particle diameter of 0.1-0.15 micrometer, it was difficult for the tendency of the needlelike nature fall by the temperature rise of reduced temperature to be much more remarkable, and to obtain the coercive force more than 1650 Oe, and a good remanence ratio in dispersibility and the moderate range of the quantity of the agent for heat treatment which does not spoil sigmas.
[0008]

[Problem(s) to be Solved by the Invention]This invention realizes fall of reduced temperature, and shortening of reducing time, without using nickel used as the cause of worsening SFD in the end of ferromagnetic fine metallic powder, etc., It is rare to produce collapse and weld of particle shape, and coercive force aims at offer of the manufacturing method of the ferromagnetic metal powder of the particles which were excellent in a remanence ratio and dispersibility above 1650 Oe.

[0009]

[Means for Solving the Problem]This invention persons prevent sintering at the time of carrying out heating reduction of the particle goethite with a major axis diameter of 0.2micro or less, and collapse of a skeleton in order to solve these problems, It was considered as a method of manufacturing efficiently magnetic metal powder which inherited well particle shape of starting material slack needlelike iron oxide, and after carrying out calcination reduction to near the magnetite presentation by calcinating tropicalization goethite which added fatty acid in nitrogen gas, a method of carrying out hydrogen reduction was developed.

[0010]Namely, fatty acid is made to stick to the tropicalization finishing needlelike iron oxide particle surface by mixing fatty acid and a needlelike iron oxide slurry which performed tropicalization, If hydrogen reduction is carried out after carrying out calcination reduction in 300-650 ** after shaping desiccation or in an after [a dry cracking particle size regulation] nitrogen gas air current, it will be the feature of this invention that metal powder excellent in coercive force, a remanence ratio, and SFD can be manufactured more in a short time compared with a conventional method.

[0011]Namely, this invention persons face hydrogen gas reduction of needlelike iron oxide or oxyiron hydroxide, If needlelike iron oxide or oxyiron hydroxide which adsorbed fatty acid before hydrogen gas reduction is calcinated at 300-650 ** in nitrogen gas, it will be returned near the magnetite presentation, Reducibility by reducing gas, such as subsequent hydrogen gas, improved, and it found out that that reduction of reduced temperature and shortening of reducing time are possible and improvement in coercive force, an improvement of a remanence ratio, and an improvement of SFD were possible. Although a cause by which such an effect was acquired is not necessarily in **, since fatty acid decomposes by calcination in nitrogen gas which is inactive gas and it is gently returned by generated reducing gas, It is imagined as that whose subsequent reducibility improves by the existence of Fe^{2+} with a large diffusion coefficient or a hole generated by weld and sintering of particles being prevented and being returned near the magnetite.

[0012]After carrying out a surface treatment which made a subject needlelike iron oxide or oxyiron hydroxide for Si, an aluminum compound, etc. for the purpose, such as form maintenance and prevention of sintering, in enforcement of this invention, adsorption treatment of fatty acid is performed and this is calcinated at 300-650 ** among a nitrogen gas inert atmosphere. As fatty acid to be used, caprylic acid or various fatty acid of $C_{\text{contained in palm oil18from C8}}$, capric acid, lauric acid, myristic acid, PAL thymic acid, and stearic acid are preferred. At ordinary temperature, in the case of a solid, it heats, and fatty acid is liquefied and uses it. After calcinating by an inert atmosphere and returning to near the magnetite presentation, reducing gas, such as hydrogen gas, performs heating reduction at 350-550 **, and ferromagnetic metal particles are obtained.

[0013]Obtained ferromagnetic metal particles For example, oxidation stabilizing

treatment of a wet type which carries out a dipping to organic solvents, such as toluene, and aerates oxidizing gases, such as air, Or inactive gas, such as nitrogen gas, can be aerated and stable ferromagnetic metal powder can be manufactured in the air by dry-type oxidation stabilizing treatment which increases a flow of gas of oxidizing qualities, such as air, gradually.

[0014]

[Working example]Hereafter, an working example explains this invention concretely.

[0015]Caprylic acid was added 5% at 40 ** to the slurry (16 g/l) of the goethite (Si/Fe=1.0%, aluminum/Fe=3.5%) of axial ratio 7.8 surface area [of 85 m] ^{2}/g which contains silicon and aluminum as an working-example 1. heat-resistant ingredient, and it agitated by the homomixer for 30 minutes.

[0016]This goethite was dried after granulation molding after filtration washing by the nutsche to a cylindrical crumb about 7 mm in length, and 4 mm in diameter.

[0017]20g of granulation molding goethite was supplied to the mold fixed zone furnace be 50 mm in diameter up, and it calcinated by carrying out temperature-up heating over 1 hour to 500 ** by nitrogen gas flow 0.2 Nl/min.

[0018]When some calcination products were taken out and the X diffraction was performed, the diffraction pattern corresponding to Fe_3O_4 or gamma-Fe_2O_3 was obtained. When granular material magnetic properties were measured in VSM (Toei Industry oscillatory type magnetometer), it was pHc=116 Oe, sigmas=56.8 emu/g, and sigma r/sigma s= 0.256, and since the color tone was black, generation of Fe_3O_4 was identified.

[0019]When the reduced powder obtained by hydrogen gas flow 5 Nl/min by performing hydrogen reduction for 525 ** 3 hours for 500 ** 3 hours was taken out into toluene following calcination and granular material magnetic properties were measured, it was pHc=1603 Oe and sigmas(Fe) =195 emu/gFe, and reduction was good. Air-drying magnetic metal powder was obtained for toluene on metal bats. When the magnetic properties of the air-dried product were measured, they were pHc=1710 Oe, sigmas=118.9 emu/g, and sigma r/sigma s= 0.536.

[0020]A 30,000 times as many electron microscope photograph as the magnetic-metal-powder particles obtained by this example is shown in Fig. 1. Needlelike nature is kept good and it turns out that there are also few weld particles. As a result of measuring the sheet characteristic, they were Sq=0.768, SFD=0.547, and 60 degree-60 degree gross =69%. The measurement result of these weighted solidity was shown in the 1st table with the comparative example.

[0021]It experimented on the same conditions as working-example 1. except not having added comparative example 1. caprylic acid. By nitrogen gas flow 0.2 Nl/min, to 500 **, it heated with the heating rate of 1 hour, and calcinated cumulatively. When some calcination products were taken out and the X diffraction was performed, the diffraction pattern of alpha-Fe_2O_3 was obtained. When granular material magnetic properties were measured in VSM, it was pHc=257 Oe, sigmas=7.3 emu/g, and sigma r/sigma s= 0.392, and the color was red.

[0022]When the reduced powder obtained by hydrogen gas flow 5 Nl/min by performing hydrogen reduction for 525 ** 3 hours for 500 ** 3 hours was taken out into toluene following calcination and granular material magnetic properties were measured, they were pHc=1520 Oe and sigmas(Fe) =180.9 emu/gFe. Air-drying magnetic metal powder

was obtained for toluene on metal bats. When magnetic properties were measured, they were pHc=1613 Oe, sigmas=113.1 emu/g, and sigma r/sigma s= 0.512.
[0023]A 30,000 times as many electron microscope photograph as the obtained magnetic-metal-powder particles is shown in Fig. 2. As compared with the magnetic metal powder of working-example 1. which added caprylic acid, needlelike nature is a little inferior and it turns out that it is not few to weld particles, either. As a result of measuring the sheet characteristic, they were Sq=0.735, SFD=0.676, and 60 degree-60 degree gross =59%.
[0024]It experimented on the same conditions as working-example 1. except having made low working-example 2. reduced temperature.
[0025]It calcinated by heating with the heating rate of 1 hour to 500 ** by nitrogen gas flow 0.2 Nl/min. When the part was taken out and the X diffraction was performed, the diffraction pattern of Fe_3O_4 or gamma-Fe_2O_3 was obtained. When granular material magnetic properties were measured in VSM, it was pHc=106 Oe, sigmas=51.1 emu/g, and sigma r/sigma s= 0.227, and since the color was black, it judged with Fe_3O_4 existing.
[0026]When the reduced powder obtained by hydrogen gas flow 5 Nl/min by performing hydrogen reduction for 475 ** 6 hours for 450 ** 3 hours was taken out into toluene following calcination and granular material magnetic properties were measured, they were pHc=1529 Oe and sigmas(Fe) =188.6 emu/gFe. Air-drying magnetic metal powder was obtained for toluene on metal bats. When magnetic properties were measured, they were pHc=1651 Oe, sigmas=110.8 emu/g, and sigma r/sigma s= 0.542.
[0027]A 30,000 times as many electron microscope photograph as the magnetic-metal-powder particles obtained by this example is shown in Fig. 3. Needlelike nature is kept good and it turns out that there are also few weld particles. As a result of measuring the sheet characteristic, they were Sq=0.781, SFD=0.547, and 60 degree-60 degree gross =70%.
[0028]It experimented on the same conditions as working-example 2. except not having added comparative example 2. caprylic acid. By nitrogen gas flow 0.2 Nl/min, to 500 **, it heated with the heating rate of 1 hour, and calcinated cumulatively. When some calcination products were taken out and the X diffraction was performed, the diffraction pattern of alpha-Fe_2O_3 was obtained. When granular material magnetic properties were measured in VSM, it was pHc=306 Oe, sigmas=1.6 emu/g, and sigma r/sigma s= 0.371, and the color was red.
[0029]When the reduced powder obtained by hydrogen gas flow 5 Nl/min by performing hydrogen reduction for 475 **-6 hours for 450 **-3 hours was taken out into toluene following calcination and granular material magnetic properties were measured, they were pHc=1522 Oe and sigmas(Fe) =180.5 emu/gFe.
[0030]Air-drying magnetic metal powder was obtained for toluene on metal bats. When magnetic properties were measured, they were pHc=1610 Oe, sigmas=106.0 emu/g, and sigma r/sigma s= 0.516.
[0031]As a result of measuring the sheet characteristic, each is inferior to the weighted solidity of the product of working-example 2. with Sq=0.746, SFD=0.606, and 60 degree-60 degree gross =54%.
[0032]Although comparative example 3. caprylic acid was added, it calcinated in the air and caprylic acid was burned, and what removed carbon was used. Other conditions were made into the same conditions as working-example 1.
[0033]It heated with the heating rate of 1 hour to 500 ** by nitrogen gas flow 0.2 Nl/min,

and calcinated cumulatively, and when some calcination products were taken out and the X diffraction was performed, the diffraction pattern of alpha-Fe $_2O_3$ was obtained. When granular material magnetic properties were measured in VSM, they were pHc=443 Oe, sigmas=1.0 emu/g, and sigma r/sigma s= 0.393.

[0034]Hydrogen reduction was performed by hydrogen gas flow 5 Nl/min for 525 ** 3 hours for 500 ** 3 hours following calcination. When the obtained reduced powder was taken out into toluene and ** object magnetic properties were measured, they were pHc=1503 Oe and sigmas(Fe) =191.2 emu/gFe. Air-drying magnetic metal powder was obtained for toluene on metal bats. When magnetic properties were measured, they were pHc=1642 Oe, sigmas=121.0 emu/g, and sigma r/sigma s= 0.528.

[0035]As a result of measuring the sheet characteristic, they were Sq=0.750, SFD=0.628, and 60 degree-60 degree gross =64%. Although reducibility was good like working-example 1., a crystallite diameter was large and Sq and SFD were inferior.

[0036]Except having made comparative example 4. reducing time 6 hours long, caprylic acid was not added like comparative example 1., but it experimented. Hydrogen reduction was performed by hydrogen gas flow 5 Nl/min for 525 ** 9 hours for 500 ** 3 hours following the same calcination as working-example 1. and comparative example 1. When obtained reduced powder was taken out into toluene and granular material magnetic properties were measured, it is pHc=1472Oe and sigmas(Fe) =191.4 emu/gFe, and was returned to a reduction degree comparable as working-example 1. Air-drying magnetic metal powder was obtained for toluene on metal bats. When magnetic properties were measured, they were pHc=1594 Oe, sigmas=121.6 emu/g, and sigma r/sigma s= 0.505. A crystallite diameter (Dx) was 165 A and was large compared with working-example 1.

[0037]As a result of measuring the sheet characteristic, it is inferior to weighted solidity of a product of Sq=0.721, SFD=0.695, and 60 degree-60 degree gross =50% and working-example 1.

[0038]Except having made comparative example 5. reducing time 9 hours long, caprylic acid was not added like comparative example 2., but it experimented. Hydrogen reduction was performed by hydrogen gas flow 5 Nl/min for 475 **-15 hours for 450 **-3 hours following the same calcination as working-example 2. and comparative example 2. When obtained reduced powder was taken out into toluene and granular material magnetic properties were measured, it is pHc=1500 Oe and sigmas(Fe) =188.8 emu/gFe, and was returned to a reduction degree comparable as working-example 2. Air-drying magnetic metal powder was obtained for toluene on metal bats. When magnetic properties were measured, they were pHc=1611 Oe, sigmas=113.3 emu/g, and sigma r/sigma s= 0.523. A crystallite diameter (Dx) was 141 A and was large compared with working-example 2.

[0039]As a result of measuring the sheet characteristic, it is inferior to weighted solidity of a product of Sq=0.758, SFD=0.611, and 60 degree-60 degree gross =57% and working-example 2.

[0040]

[Table 1]

第１表

	還元度	粉体特性						シート特性			
	σs(Fe)	pHc	σs	σr/σs	Dx	SSA	sHc	Sq	SFD	OR	gloss
	emu/gFe	Oe	emu/g	-	A	m^2/g	Oe	-	-	-	%
実施例１	195.4	1710	118.9	0.536	138	67.0	1680	0.768	0.547	1.79	69
実施例２	188.6	1651	110.8	0.542	131	66.4	1626	0.781	0.547	1.83	70
比較例１	180.9	1613	113.1	0.512	163	59.9	1593	0.735	0.676	1.69	59
比較例２	180.5	1610	106.0	0.516	143	64.9	1608	0.746	0.606	1.71	54
比較例３	191.2	1642	121.0	0.528	155	59.9	1615	0.750	0.628	1.69	64
比較例４	191.4	1594	121.6	0.505	165	57.6	1600	0.721	0.695	1.58	50
比較例５	188.8	1611	113.3	0.523	141	62.0	1610	0.758	0.611	1.73	57

CLAIMS

[Claim(s)]

[Claim 1]A manufacturing method of ferromagnetic metal powder facing manufacturing metallic magnetic powder which makes iron or iron a subject by using as a raw material needlelike goethite which performed tropicalization, adding fatty acid beforehand, and carrying out heating reduction in a reducing atmosphere.

[Claim 2]A manufacturing method of ferromagnetic metal powder given in the 1st clause of a claim calcinating under a 300-650 ** inert gas atmosphere, and performing calcination reduction before carrying out heating reduction.

[Claim 3]Fatty acid to add Caprylic acid, lauric acid, myristic acid, PAL thymic acid, The 1st clause of a claim that is one sort or acid beyond it chosen from a group which consists of stearic acid, capric acid, and various fatty acid of C_8 to C_{18} contained in palm oil, or a manufacturing method of ferromagnetic metal powder given in the 2nd clause.

[Claim 4]A manufacturing method of ferromagnetic metal powder of the 1st clause of a claim - the 3rd clause carrying out covering processing of Si compound and the aluminum compound as a tropicalization agent at needlelike goethite given in any 1 clause.

[Claim 5]A manufacturing method of ferromagnetic metal powder of the 1st clause of a claim - the 4th clause whose Al quantity of 0.5 to 2% and an aluminum compound the amount of Si of Si compound used as a tropicalization agent is 2.5 to 5% to Fe to Fe given in any 1 clause.

[Claim 6]A manufacturing method of ferromagnetic metal powder of the 1st clause of a range of claim for patent, wherein reduced temperature is 350-550 ** - the 5th clause

given in any 1 clause.
[Claim 7]A manufacturing method of ferromagnetic metal powder of the 1st clause of a claim - the 6th clause whose long axis length of needlelike goethite is at least 0.3 micrometer or less given in any 1 clause.
[Claim 8]A manufacturing method of ferromagnetic metal powder of the 1st clause of a claim - the 7th clause whose addition of fatty acid is 2 to 10% of needlelike goethite given in any 1 clause.
[Claim 9]A manufacturing method of ferromagnetic metal powder of the 1st clause of a claim - the 8th clause whose reducing atmosphere is hydrogen gas atmosphere given in any 1 clause.
[Claim 10]A manufacturing method of ferromagnetic metal powder of the 2nd clause of a claim - the 9th clause whose inactive gas is nitrogen given in any 1 clause.